

CHEMICAL AND MORPHOLOGICAL CHANGES OF REUSABLE SURFACE INSULATION  
COATINGS AS A FUNCTION OF CONVECTIVELY HEATED CYCLIC TESTING

by

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## ABSTRACT

The effects of convective heating upon reusable surface insulation coatings were studied utilizing scanning electron microscopy, X-ray fluorescence, and X-ray diffraction. Samples of coated LI-1542, HCF-MOD III and REI-MOD 1A were cycled in an arc plasma stream up to 15 times for 15 minutes per cycle at surface temperatures simulating those on the space shuttle vehicle in areas 2 and 2P as defined by the NASA-MSC.

The scanning electron microscope with an X-ray fluorescence analysis attachment was used to examine chemical and morphological changes in the insulation coating surfaces. The surfaces of REI-MOD 1A and HCF-MOD III coatings were roughened substantially by the convectively heated environment while the LI-1542 was significantly smoothed after testing. Most of the observed changes in morphology were almost complete within one cycle in REI-MOD 1A and LI-1542. The HCF-MOD III coating exhibited much more gradual changes. These gradual changes were due in part to the growth of an apparently new morphological phase out of the coating. Scanning electron microscopy also showed surface cracking of varying degrees in all of the coatings. The surface chemistry of the coatings as examined by X-ray fluorescence revealed that significant changes in composition were occurring during cycling, particularly within the HCF-MOD III coating, to a lesser extent within the REI-MOD 1A coating, while smaller changes in composition were observed in LI-1542. In order to evaluate the significance of the surface chemistry changes observed, scanning electron micrographs were taken of representative cross-sections of REI-MOD 1A and HCF-MOD III before and after testing, with concurrent analysis by X-ray fluorescence.

## INTRODUCTION

This paper describes the results of a test program initiated to evaluate the response and stability in convective heating of reusable surface insulation (RSI). These data are required to define RSI's reusability during its proposed 100-mission lifetime as the thermal protection system on space shuttle. The paper describes the response of RSI to both convective and radiative heating environments in terms of the chemical changes in the coatings that occur. It also describes the morphological changes that occur during arc plasma testing. The testing methods and optical property variations after testing are described in another paper in this volume of the Proceedings entitled, "Cyclic Arc Plasma Tests of RSI Materials Using a Preheater," by D.A. Stewart.

The model configuration and analysis techniques are described first. Changes in coating morphology of HCF-MOD III, LI-1542, and REI-MOD 1A at two heating rates are then described followed by a discussion of the changes in surface chemistry that occur during these tests. Subsequently, the surface chemistry changes observed are compared to similar data obtained from radiantly heated coatings and the significance of the difference between the results are discussed. Finally, the changes in chemistry of the coatings in cross section before and after convectively heated cyclic testing are discussed and the significance of surface chemistry changes described.

## RSI SAMPLES BEFORE AND AFTER ARC-PLASMA TESTING

(Figure 1)

The model configuration used in the investigation is shown in this figure. It consisted of nine, 40° reusable surface insulation (RSI) segments. The three RSI's studied, REI-MOD 1A mullite, HCF-MOD III mullite, and LI-1542 silica are shown in this figure before and after testing in the arc plasma environment. Each sample was subjected to a different number of convectively heated cyclic tests. Most of the results presented will be for a 340 kw/m<sup>2</sup> heating rate although some results at a 450 kw/m<sup>2</sup> heating rate are also presented. Comparisons will be shown of the results from convective heating with those of a radiantly heated test series at the same surface temperature and static pressure. The most obvious changes which occur in the coatings tested are changes in color. Other changes, some of which explain the color changes observed, are presented in the following figures.

The coatings studied have the following initial compositions:\*

(1) The LI-1542 coating designated as 0042, consists of a densified silica sublayer with a borosilicate glass sealer overlayer. The borosilicate glass sealer is approximately 96% SiO<sub>2</sub>, 3% B<sub>2</sub>O<sub>3</sub> and 1% other oxides, and contains particulate silicon carbide as an emittance pigment.

(2) The HCF-MOD III coating designated as M5<sub>23</sub>A7P700 is multilayered, having a dense mullite sublayer, a borosilicate chromium oxide intermediate layer acting as a diffusion barrier, and a high emittance top layer consisting of iron, cobalt, and chromium oxides (P700) bonded together with a potassium silicate glass.

(3) The REI-MOD 1A coating designated as SR2/XSR2 is made up of a densified sublayer and an outer coating of kyanite/petalite in a glass matrix. Both layers have the same matrix composition, that is, Li<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>. Nickel oxide is added as an emittance pigment.

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\* A more complete description of each coating studied can be found in the final reports<sup>1,2,3</sup> submitted by each contractor.

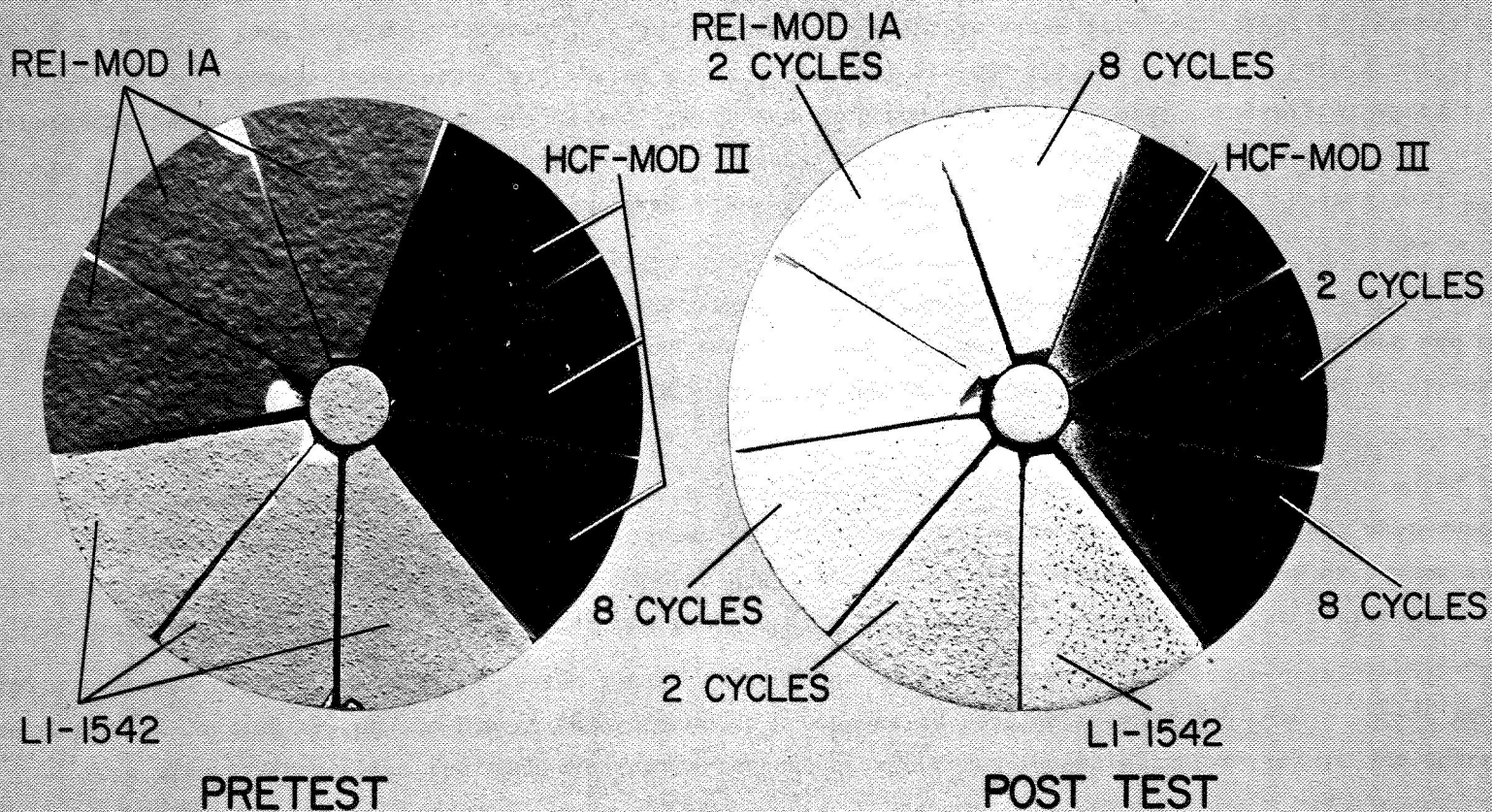


# RSI SAMPLES BEFORE AND AFTER ARC-PLASMA TESTING

$$\dot{q}_{cw} = 340 \text{ kW/m}^2$$

$$H_{e0} = 10.4 \text{ MJ/kg}$$

$$P_s = 810 \text{ N/m}^2$$



0.5  
mm

Figure 1

## SCANNING ELECTRON MICROGRAPHS OF RSI COATINGS AS A FUNCTION OF CYCLIC ARC PLASMA TESTING

(Figure 2)

This figure illustrates the morphological structure of the three reusable surface insulation coatings before and after testing in the arc plasma environment at a convective heating rate of  $340 \text{ kw/m}^2$ . Since each coating's reaction to the convectively heated cyclic testing was unique they will be discussed separately.

The LI-1542 coating, which exhibited the least change as a result of exposure to the environment, is transformed within one cycle from a very rough bubbled glass surface to a relatively smooth one with some small cavities. Subsequent cycling of this coating produced little effect except to cause a less glassy appearance of the coating. Because of this, no other scanning electron micrographs of this coating will be presented in subsequent figures.

The REI-MOD 1A coating was affected significantly by the cyclic testing in the arc plasma environment. The coating transformed from a relatively smooth surface to a much rougher one with a foamy appearance and many attached and unattached lumps within one cycle. Continued cycling caused the surface to become smoother again by apparently flattening out the lumps present after the first test cycle.

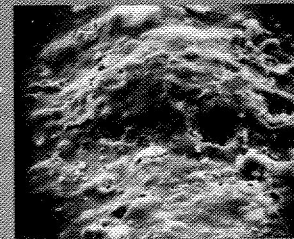
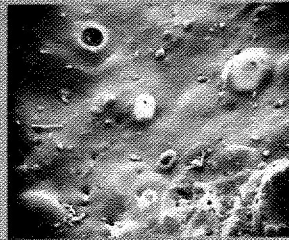
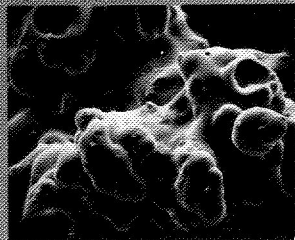
The HCF-MOD III coating exhibited the most significant reaction to the convectively heated cyclic tests. It transformed from a relatively smooth particulate surface to a much rougher one with many new characteristic features evident within one cycle. These new features included a coral like morphological phase\* and small areas of exposed glassy sublayer. After eight additional cycles, the coral grew in both diameter and height, but the area they covered decreased. In addition, a dendritic glass structure appeared between the coral and the significantly larger exposed glass sublayer.

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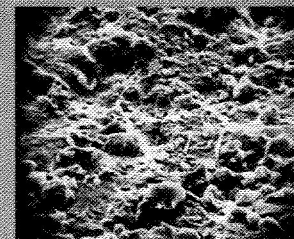
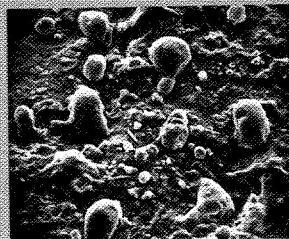
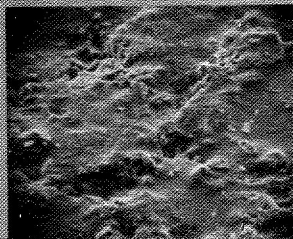
\* Subsequent discussion of this phase will refer to it only as coral.

# SCANNING ELECTRON MICROGRAPHS OF RSI COATINGS AS A FUNCTION OF CYCLIC ARC PLASMA TESTING

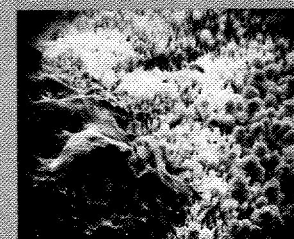
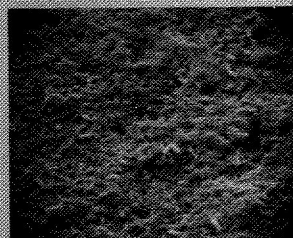
500 x,  $\dot{q}_{cw} = 340 \text{ kw/m}^2$



(a) LI-I542,  $T_w = 1422^\circ\text{K}$



(b) REI-MOD IA,  $T_w = 1450^\circ\text{K}$



PRETEST

1 CYCLE

9 CYCLES

(c) HCF-MOD III,  $T_w = 1550^\circ\text{K}$

100  $\mu$

Figure 2

## SCANNING ELECTRON MICROGRAPHS OF HCF-MOD III COATING AS A FUNCTION OF CYCLIC ARC PLASMA TESTING

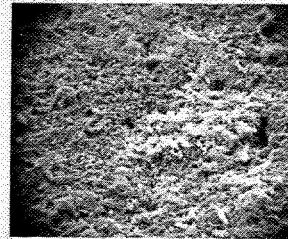
(Figure 3)

858 This figure illustrates the morphological structure of the HCF-MOD III coating during the cyclic arc plasma tests. These tests were performed at heating rates of  $340 \text{ kw/m}^2$  and  $450 \text{ kw/m}^2$ . The response of the HCF-MOD III coating to these heating rates differed only in the rate of transition from the initially smooth surface to the final result. At the lower heating rate the reaction proceeds very gradually after the initial transition. After one cycle it is multicracked and very rough, and we see the newly formed coral phase, a cobalt iron oxide spinel. After one cycle the coral have a very loosely defined structure and cover a majority of the surface. The cracks and holes between the coral cover the remainder of the surface and expose the glassy sublayer below the surface layer. After three cycles the coral have grown significantly in both height and diameter and their overall structure is more clearly defined. In addition, the glassy areas exposed between the coral have expanded to cover a larger portion of the total surface of the coating. After six cycles the coral show continued growth in both height and diameter and the glassy areas have grown larger. The transition areas between the coral and the glassy areas have become more evident. The majority of the glassy areas appear less fluid, indicating an apparent loss of components of the original glass. At nine cycles the same trends have continued with the coral growing in height and slightly in diameter, and the glassy areas continuing to spread out and cover more of the total surface.

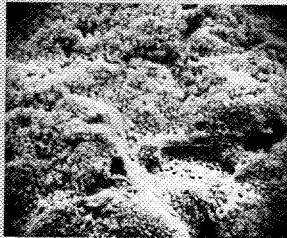
At the higher heating rate,  $450 \text{ kw/m}^2$ , the coating changes much more rapidly. After one cycle, for example, the coral have already grown to the same size as those produced after nine cycles at the lower heating rate. The glassy areas exposed between the coral have already begun covering a significant portion of the total surface. At three cycles, the glassy areas have become extensive and the coral have receded significantly. After six cycles the glassy areas are beginning to roughen up considerably while the coral are rapidly receding. At nine cycles the coral exist only in limited areas and the sublayer is extremely rough. This result indicates the reaction has proceeded much further at the higher heating rate than it did at the lower heating rate.



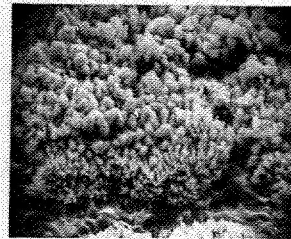
# SCANNING ELECTRON MICROGRAPHS OF HCF-MOD III COATING AS A FUNCTION OF CYCLIC ARC PLASMA TESTING



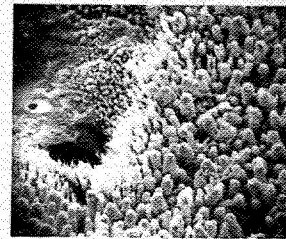
PRETEST



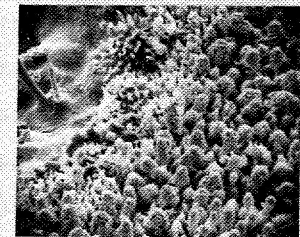
1 CYCLE



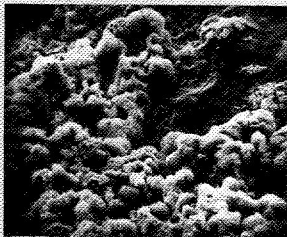
(a)  $\dot{q}_{cw} = 340 \text{ kw/m}^2$ ,  $T_w = 1550^\circ \text{K}$



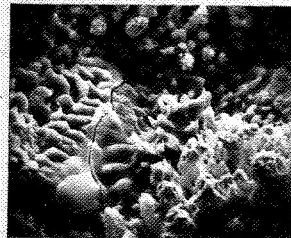
6 CYCLES



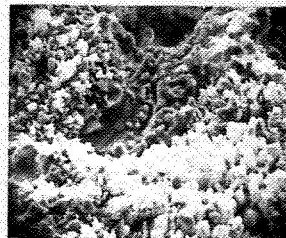
9 CYCLES



100  $\mu$



3 CYCLES



(b)  $\dot{q}_{cw} = 450 \text{ kw/m}^2$ ,  $T_w = 1630^\circ \text{K}$

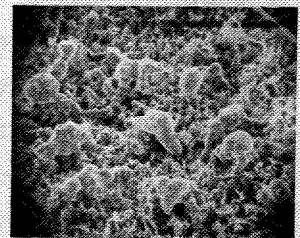


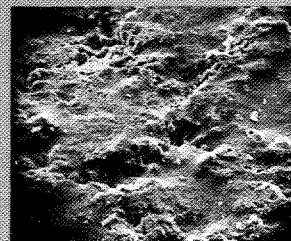
Figure 3

## SCANNING ELECTRON MICROGRAPHS OF REI-MOD 1A COATING AS A FUNCTION OF CYCLIC ARC PLASMA TESTING

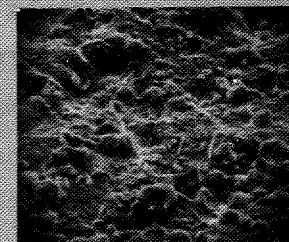
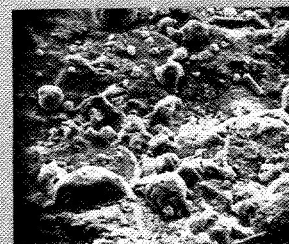
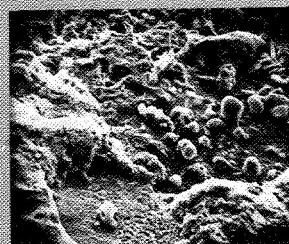
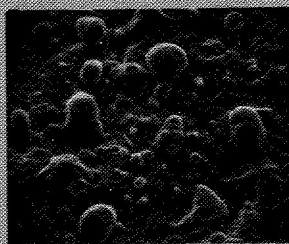
(Figure 4)

808  
The morphological structure of the REI-MOD 1A coating as a function of convectively heated cyclic testing at the two heating rates is illustrated in this figure. The reaction of this coating to the cyclic testing was very similar at both of the heating rates. The end result appears morphologically equivalent. The only difference of note is in the initial stages at the lower heating rate. The transition from the initial surface is more clearly seen here than it is at the higher heating rate. The response of the coating at the lower heating rate clearly indicates that there are two steps to the transition. During the initial step of the transition the virgin surface, which is relatively smooth with some cubic crystallites visible, is transformed into a very rough, foamy surface that has apparently balled up in one cycle. This very rough surface becomes significantly smoother by apparently fusing and flattening out with continued cycling at the lower heating rate. The concentration of spherical particulates on the surface also decreases with continued cycling until after nine cycles they have completely disappeared. At this point the surface appears much like it does after one cycle of testing at the higher heating rate. At the higher heating rate the first step in the transition has apparently occurred prior to the end of the first cycle. After the first cycle of testing little change in surface morphology is evident.

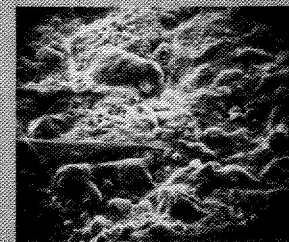
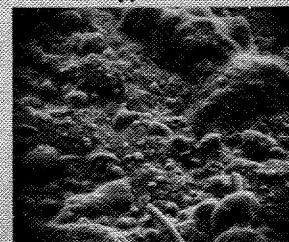
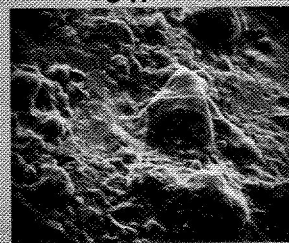
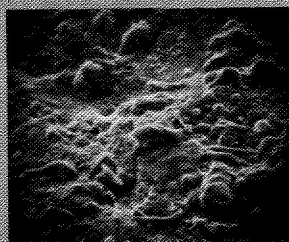
# SCANNING ELECTRON MICROGRAPHS OF REI-MOD 1A COATING AS A FUNCTION OF CYCLIC ARC PLASMA TESTING



PRETEST



(a)  $\dot{q}_{cw} = 340 \text{ kW/m}^2$ ,  $T_w = 1450^\circ\text{K}$



1 CYCLE

3 CYCLES

6 CYCLES

9 CYCLES

(b)  $\dot{q}_{cw} = 450 \text{ kW/m}^2$ ,  $T_w = 1483^\circ\text{K}$

100  $\mu$

Figure 4

## SCANNING ELECTRON MICROGRAPHS OF CROSS SECTION OF RSI COATINGS BEFORE AND AFTER ARC PLASMA TESTING

(Figure 5)

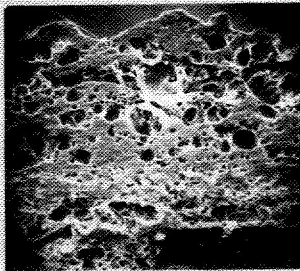
The response of RSI coatings to convective heating is illustrated in this figure, which shows cross sections of each coating before and after cyclic testing. Each coating's response to the environment was unique. The LI-1542 coating exhibited the most porosity both before and after eight cycles of testing at the  $340 \text{ kw/m}^2$  heating rate, even though the amount of porosity had decreased with testing. The change in surface morphology of this coating during convective heating, noted previously, is also evident in the cross sectional photomicrographs. The REI-MOD 1A coating appears very uniformly dense with some porosity before test. After eight cycles of testing little change is evident except in the uniformity of the coating. Near the surface of the coating a thin layer has formed after test that appears to be different from the rest of the coating. This difference results in a lighter appearance of the coating in the scanning electron microscope and may be caused either by foaming, which makes the coating appear less dense, or by the loss of some elemental component, which makes it appear lighter after test. The HCF-MOD III coating exhibited the most significant response to the convectively heated environment. It is different from the other coatings studied, since it is obviously multilayered. The surface layer before test is primarily a particulate material held together with a glassy binder. The sublayers contain chromia grains, have some porosity and are glassy in appearance before test. After eight cycles there is an apparent loss of the particulate top layer indicating some surface recession has occurred. The coral (described previously in figure 2) are the only remaining part of that initial top layer. The remainder of the coating's sublayers appear to be unaffected by the environment.



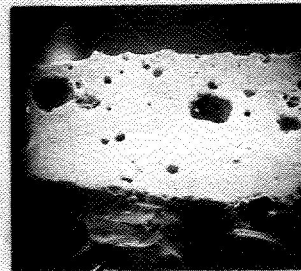
# SCANNING ELECTRON MICROGRAPHS OF CROSS SECTION OF RSI COATINGS BEFORE AND AFTER ARC PLASMA TESTING

190x

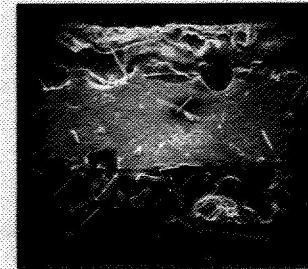
LI 1542



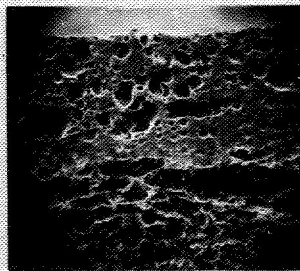
REI-1A



HCF-III

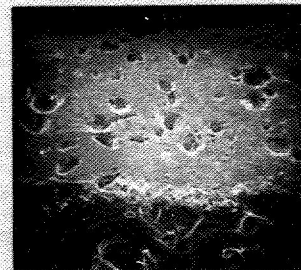


PRETEST

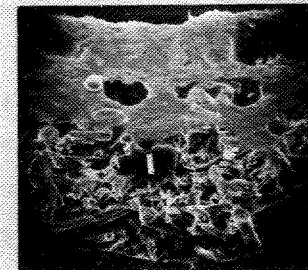


$T_w = 1422^\circ\text{K}$

400  $\mu$



$T_w = 1450^\circ\text{K}$



$T_w = 1550^\circ\text{K}$

8 CYCLES,  $\dot{q}_{cw} = 340 \text{ KW/m}^2$

Figure 5

## X-RAY FLUORESCENCE PATTERNS OF HCF-MOD III COATING

(Figure 6)

In order to obtain data on the chemical changes of the coatings studied as a function of cyclic arc plasma testing, an energy dispersive X-ray analysis (EDX) unit attached to the scanning electron microscope was used. This unit determines the elements present by X-ray fluorescence analyses. The elements are differentiated by the characteristic wavelengths or excitation voltages of the X-rays they emit when bombarded by electrons within the scanning electron microscope. The EDX unit was used in two different modes of operation. In the first mode, the location of an element present in oxide form in the coating could be established. The form of the data obtained in this mode was a dot pattern. This pattern was obtained by taking a photograph of an oscilloscope display which showed a white dot wherever X-rays of the correct excitation voltage were detected as the scanning electron microscope scanned across the surface. Subsequently, a scanning electron micrograph was taken of the same area from which the dot pattern was obtained to establish the location of the element. In the second mode, which will be described later, the EDX unit integrates all of the dot patterns to obtain a complete semi-quantitative X-ray fluorescence analysis.

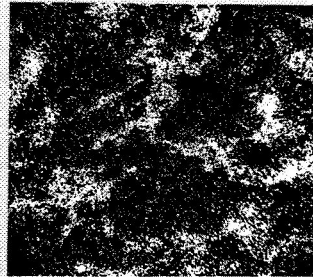
The photographs shown in figure 6 present some of the data obtained from the EDX unit in the first mode. It illustrates a scanning electron micrograph of the surface of the HCF-MOD III coating after nine cycles at the  $340 \text{ kw/m}^2$  heating rate along with dot patterns for the elements of interest. It indicates that the elements on the surface of the HCF-MOD III coating are segregated with cobalt and iron being present in coralloid areas and silicon being the primary component of the phase in between. Chromium appears to be uniformly distributed. This type of analysis was used primarily for RSI coatings in cross section.

# X-RAY FLUORESCENCE PATTERNS OF HCF-MOD III COATING

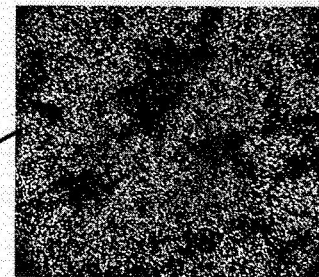
$$\dot{q}_{cw} = 340 \text{ kw/m}^2$$

9 CYCLES

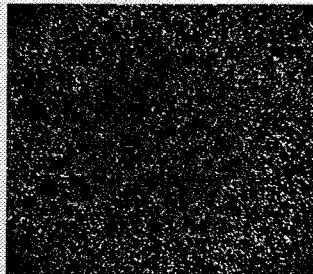
50 x



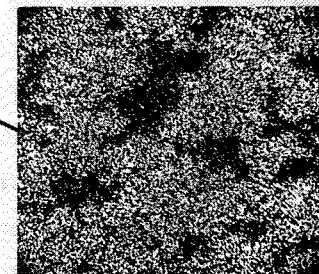
SILICON



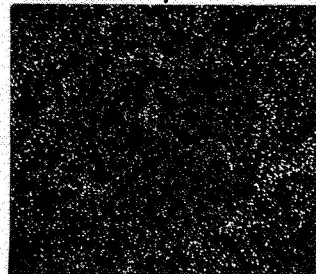
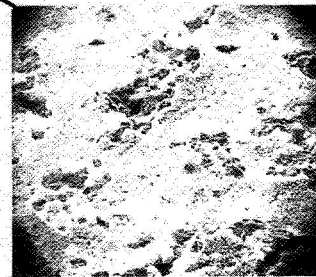
COBALT



CHROMIUM



IRON



POTASSIUM

1000  $\mu$

Figure 6

## SCHEMATIC OF DENSITOMETER EQUIPMENT

(Figure 7)

866  
In the first mode of operation, the spatial distribution and relative amount of each element present in different layers of the coating were determined using a modified densitometer as schematically illustrated in figure 7. These data could then be used to determine if components of the coating were diffusing into the insulation itself or toward the surface of the coating with cyclic testing in the arc plasma environment. As the figure shows, a collimated beam of light is passed through a portion of a negative of the dot pattern of interest, and the intensity of the transmitted beam is measured with a photomultiplier tube. The dot pattern of interest is moved at a constant rate across the stationary 0.635 cm (1/4 inch) square beam so that a plot is produced of total intensity of the transmitted beam versus the distance traveled across the negative of the dot pattern. The optical system, which is unique to this equipment, diffuses and then concentrates the transmitted image of the square beam passed through the dot pattern. The output from the photomultiplier is a total intensity for the transmitted beam which represents the averaged or integrated dot density within the area of the negative the beam passed through. This plot obtained from the strip chart recorder is a semi-quantitative representation showing the location and concentration of the element of interest. This type of analysis for the elements present will be illustrated for cross sections of the HCF-MOD III and REI-MOD 1A coating before and after testing in the convectively heated environment. No patterns of the LI-1542 coatings will be presented since silicon is the only element detectable in it with this analytical technique.

# SCHEMATIC OF DENSITOMETER EQUIPMENT

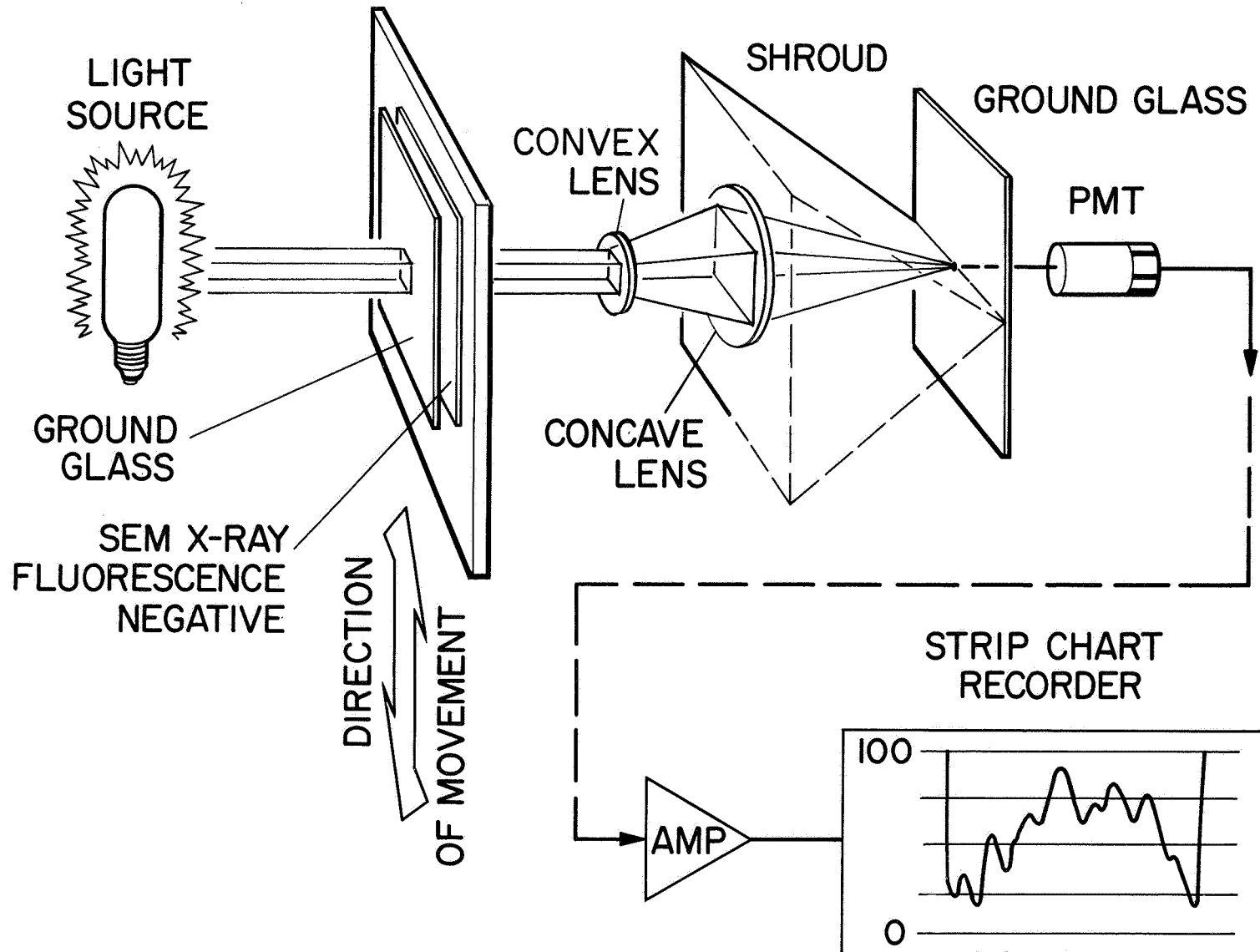


Figure 7

## X-RAY FLUORESCENCE ANALYSIS OF HCF-MOD III COATING

(Figure 8)

898

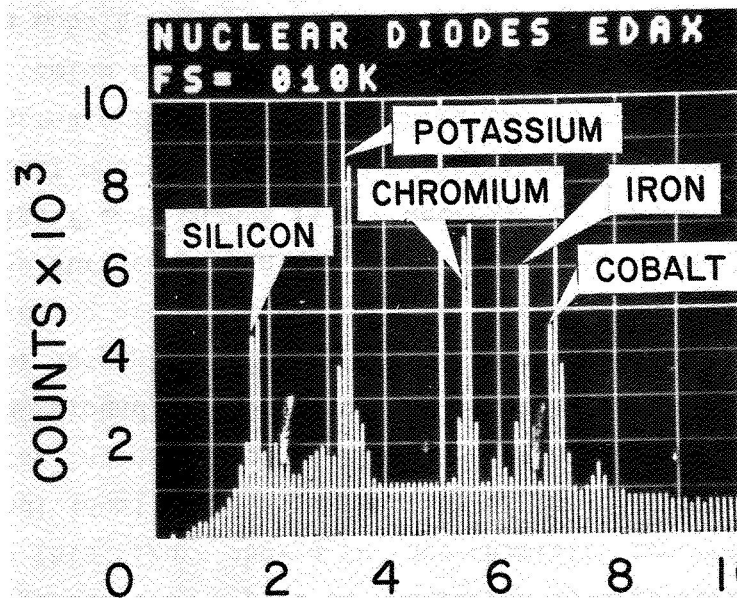
This figure illustrates an X-ray fluorescence analysis of the HCF-MOD III coating before and after convectively heated cyclic testing utilizing the second mode of operation of the EDX unit. In this mode of operation the EDX unit counts all the X-rays detected and stores them according to their relative excitation voltages. This type of analysis results in a total average concentration on the surface of each element rather than the spatial distribution found with the first EDX mode. The data in this figure were obtained after counting for 40 seconds while the scanning electron microscope was scanning the surface of the HCF-MOD III coating. The peaks shown correspond to the excitation voltage of the elements identified in the pretest data. In the post test data the silicon (1.8 keV) and the iron (6.4 keV) peak intensity exceeded 10,000 counts and therefore are referred to the axis identified on the far right of the plot for their total peak intensity. These plots indicate that the surface chemistry of the HCF-MOD III coating is changing considerably with convectively heated cyclic testing. The relative concentration of silicon and iron have increased due to the depletion of potassium and chromium on the surface. The cobalt concentration appears relatively unaffected. These data also indicate the potential value of the EDX unit to determine surface chemistry changes with cyclic testing, although several limitations must be recognized before it can be used. These limitations are:

- (1) The chemical analysis obtained is from the materials lying within a half micron of the surface. This defines the meaning of surface.
- (2) The analysis is possible only for elements with an atomic number of 11 (Na) or more, primarily due to electronic noise.
- (3) The analysis is only semiquantitative.



# X-RAY FLUORESCENCE ANALYSIS OF HCF - MOD III COATING

PRETEST



POST TEST , 9 cycles

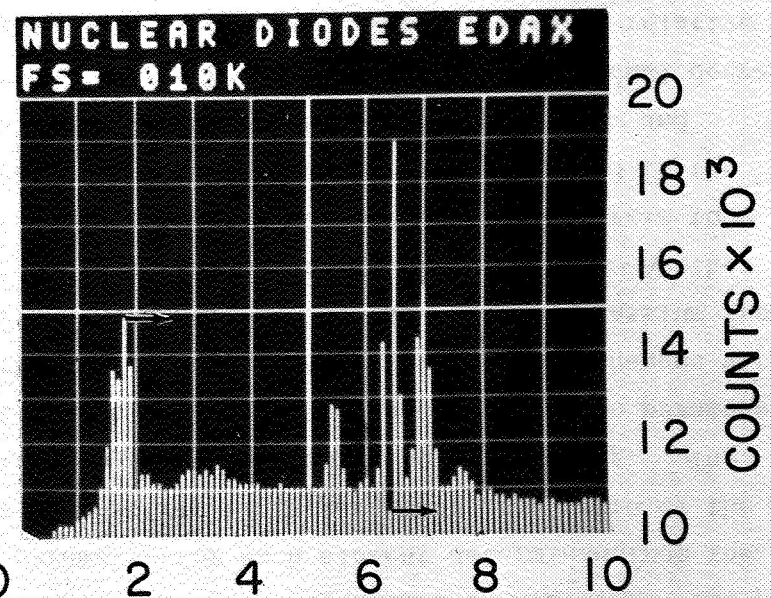


Figure 8

## CHANGE IN SURFACE COATING CHEMISTRY AFTER ARC PLASMA TESTING HCF-MOD III

(Figure 9)

The change in surface coating chemistry during convectively heated cyclic testing is shown in this figure, for the HCF-MOD III coating at the  $340 \text{ kw/m}^2$  heating rate. Each individual analysis resulted from a plot of excitation voltage versus number of counts as illustrated in figure 8. The plots in this figure show a surface chemistry concentration parameter for each element determined from the individual plots as a function of the number of cycles of testing. This parameter is a ratio of the peak intensity for an element examined to that of silicon in the same coating before testing. The background is subtracted out in each case. No correction has been made to the concentration parameter for absorption of X-rays by elements present within the surface under analysis. Several changes with cycling are indicated by this figure. The most significant change noted is the loss of potassium from the surface within one test. No change in the potassium concentration occurred thereafter. Another significant change is the decrease in concentration of chromium on the surface within one cycle to a point where it remains constant throughout the remainder of the tests. A third change noted is the increase in relative concentration of cobalt after one cycle caused by the loss of potassium and chromium coincident with the formation of coral, described in figure 2, followed by the gradual decrease in cobalt concentration, again coincident with the recession of the coral. The increase in relative concentration of iron after about three cycles, followed by its very gradual decrease in concentration, is also an apparent trend coincident with the formation and recession of coral. These trends also explain the optical property changes observed in this coating during cyclic testing reported in the paper by Stewart, presented at this symposium. The last change noted was the gradual increase in concentration of silicon due to the gradual depletion of all other elements with increasing cyclic exposure coincident with the apparent growth of glassy areas between the coral. When all these changes and trends are compared, one concludes that the more volatile oxides have decreased in concentration the fastest. Thus, the loss of potassium from the surface is the fastest followed in order by chromium, cobalt and iron. Silicon, being the most stable, actually appears to increase in concentration due to the depletion of the more volatile oxides.



# CHANGE IN SURFACE COATING CHEMISTRY AFTER ARC PLASMA TESTING

HCF-MOD III

$$\dot{q} = 340 \text{ kW/m}^2$$

$$H_{e0} = 10.7 \text{ MJ/kg}$$

$$P_s = 810 \text{ N/m}^2$$

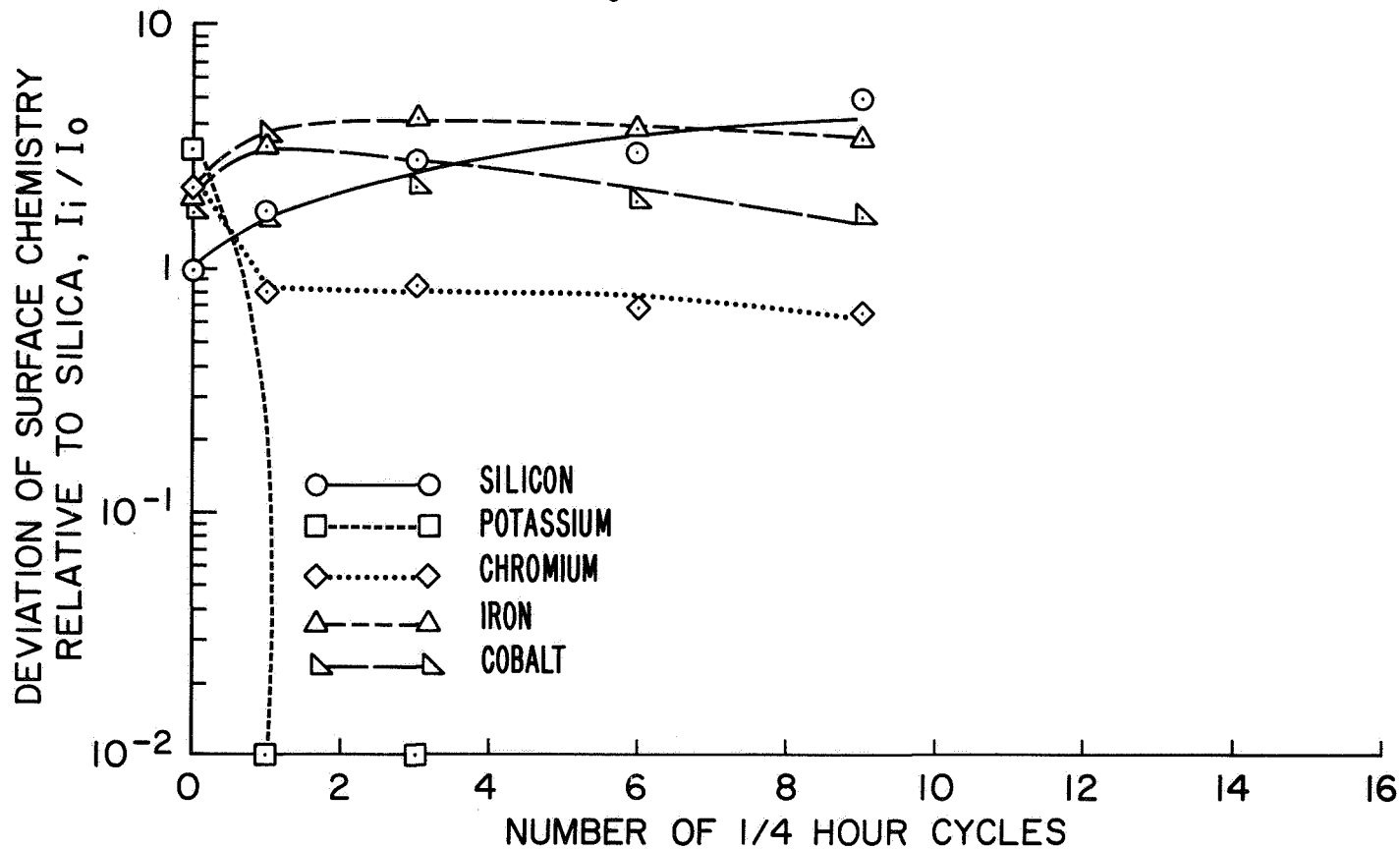


Figure 9

CHANGE IN SURFACE COATING CHEMISTRY AFTER ARC PLASMA TESTING  
HCF-MOD III

(Figure 10)

The change in surface coating chemistry is shown in this figure for the HCF-MOD III coating at the 450 kw/m<sup>2</sup> heating rate. The changes and trends noted are similar to those noted at the lower heating rate for all of the elements except chromium, which is beginning to increase in relative concentration after about 15 cycles of testing at the higher heating rate. This increased chromium concentration may be the result of exposing chromia grains present within the sublayers of the HCF-MOD III coating. Figures 9 and 10 show that the response of the coating to the convectively heated environment is apparently equivalent in terms of surface chemistry at both heating rates, although the response is accelerated at the higher heating rate.

# CHANGE IN SURFACE COATING CHEMISTRY AFTER ARC PLASMA TESTING

HCF-MOD III

$$\dot{q} = 450 \text{ kW/m}^2$$

$$H_{e0} = 15.5 \text{ MJ/kg}$$

$$P_s = 960 \text{ N/m}^2$$

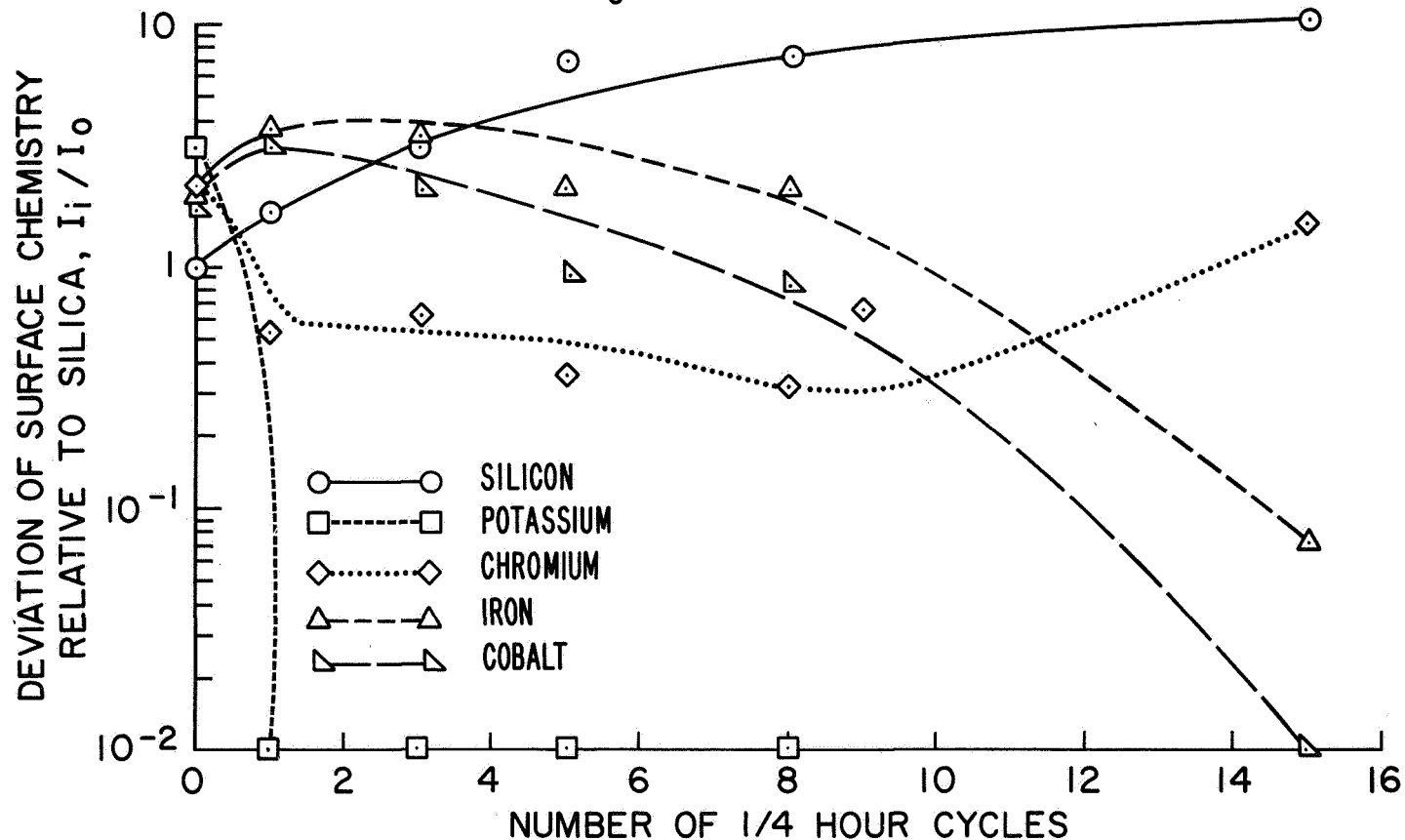


Figure 10

CHANGE IN SURFACE COATING CHEMISTRY AFTER RADIANT HEAT TESTING  
HCF-MOD III

(Figure 11)

The change in surface coating chemistry which occurs as a function of radiantly heated cyclic tests at 1480°K for the HCF-MOD III coating is illustrated in this figure. The tests were conducted at a pressure of 810 N/m<sup>2</sup> (0.008 atm), which is equivalent to the surface pressure in the convectively heated cyclic tests. The results indicate several differences in surface chemistry between the radiatively heated cyclic testing behavior and the similar convective heating test results illustrated in figure 9. Specifically the potassium concentration drops an order of magnitude further during convective heating tests than it does during radiant tests, indicating a significant enhancement of its vaporization due to the boundary layer present during convective heating. The relative concentration of chromium appears to increase slightly in radiant heating whereas it decreases during convective heating, again indicating some reaction with the boundary layer is probably occurring. The cobalt and iron concentrations appear unaffected in radiant heating whereas they change significantly in convective heating concurrent with the formation of a coralloid phase described previously. The results shown in figures 9 and 11, therefore, indicate a significant difference in the HCF-MOD III coating's chemical response to the two environments.

# CHANGE IN SURFACE COATING CHEMISTRY AFTER RADIANT HEAT TESTING

HCF - MOD III

$T_w \approx 1480^\circ \text{ K}$        $P_s = 810 \text{ N/m}^2$

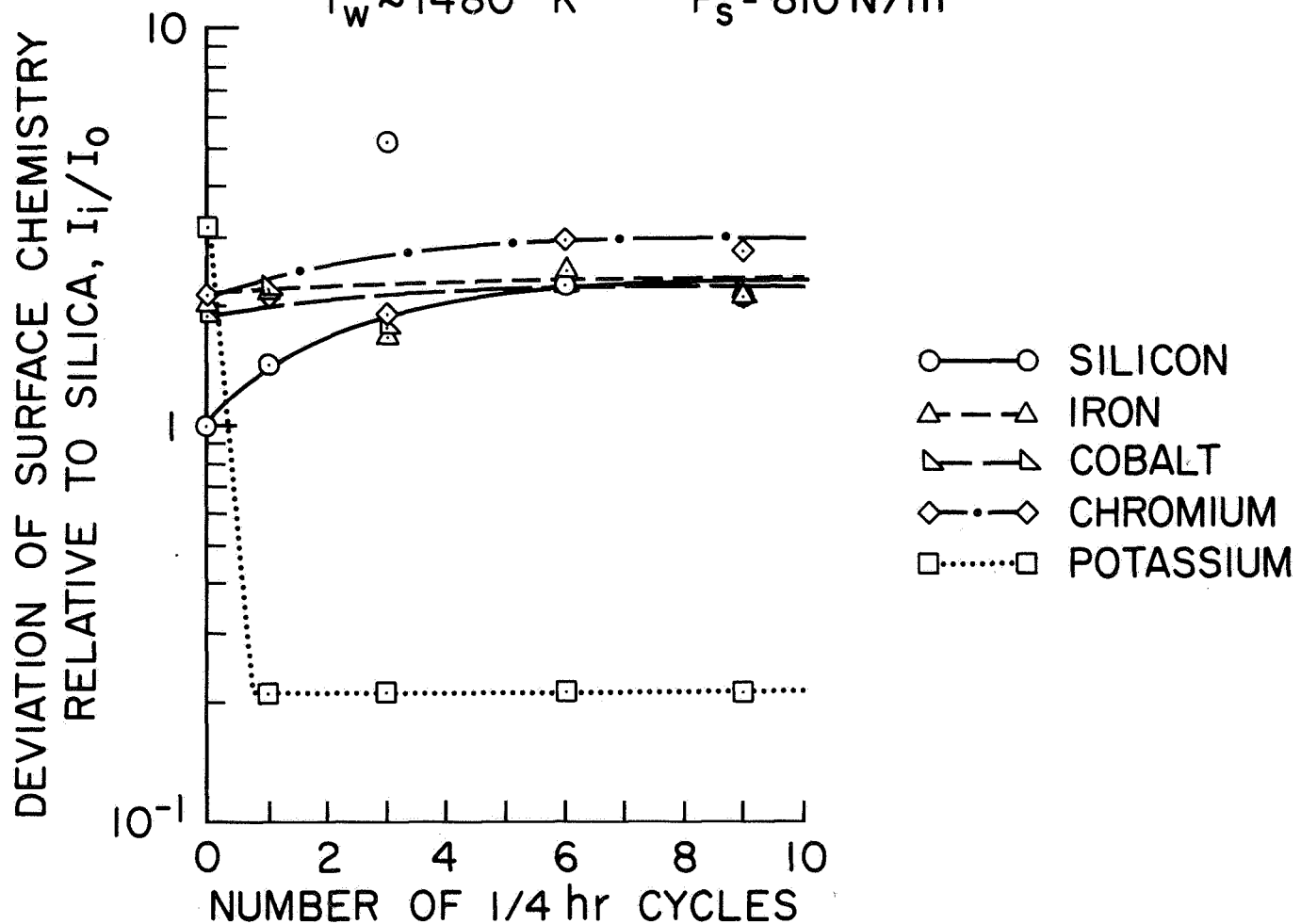


Figure 11

## CHANGE IN SURFACE COATING CHEMISTRY AFTER ARC PLASMA TESTING

REI-MOD 1A

(Figure 12)

The change in surface coating chemistry during convectively heated cyclic testing of the REI-MOD 1A coating is illustrated in this figure for the 340 kw/m<sup>2</sup> heating rate. Several changes are indicated in this figure. The first change noted is the decrease in relative surface concentration of calcium, nickel, and iron. The decrease in nickel concentration on the surface is probably the cause of the change in coating color from greenish brown before test to grayish white after one cycle noted in figure 1. Another change noted is the increase in relative concentration of the aluminum and silicon, which are relatively nonvolatile oxides, after one cycle. This change is caused by the depletion of the other elements present initially including lithium, which could not be detected in this analysis. Little change in concentration of aluminum and silicon is noted thereafter with continued cycling. Another trend noted is the gradual increase in the relative concentration of titanium, which is another of the more stable oxides.

# CHANGE IN SURFACE COATING CHEMISTRY AFTER ARC PLASMA TESTING

REI-MOD 1A

$$\dot{q} = 340 \text{ kW/m}^2$$

$$H_{e0} = 10.7 \text{ MJ/kg}$$

$$P_s = 810 \text{ N/m}^2$$

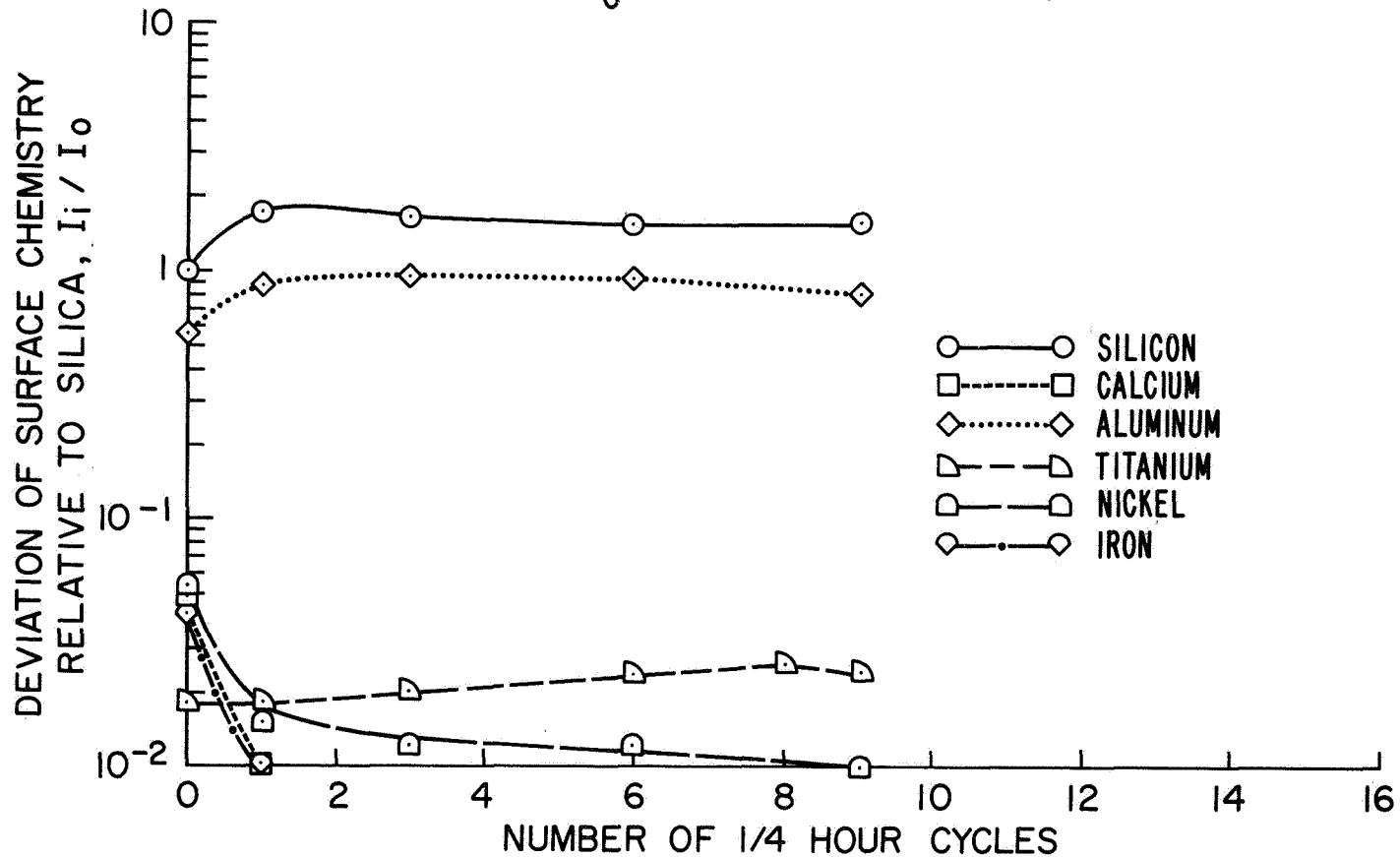


Figure 12

CHANGE IN SURFACE COATING CHEMISTRY AFTER ARC PLASMA TESTING  
REI-MOD 1A

(Figure 13)

This figure illustrates the change in surface coating chemistry during convectively heated cyclic testing of the REI-MOD 1A coating at the  $450 \text{ kw/m}^2$  heating rate. These results indicate that the changes at this heating rate are the same as those shown in the previous figure for this coating at the  $340 \text{ kw/m}^2$ . These changes also explain the optical property changes observed in the REI-MOD 1A coating as a function of cyclic convective heating tests reported in the paper by D.A. Stewart.



# CHANGE IN SURFACE COATING CHEMISTRY AFTER ARC PLASMA TESTING

REI-MOD 1A

$$\dot{q} = 450 \text{ kW/m}^2$$

$$H_{e0} = 15.5 \text{ MJ/kg}$$

$$P_s = 960 \text{ N/m}^2$$

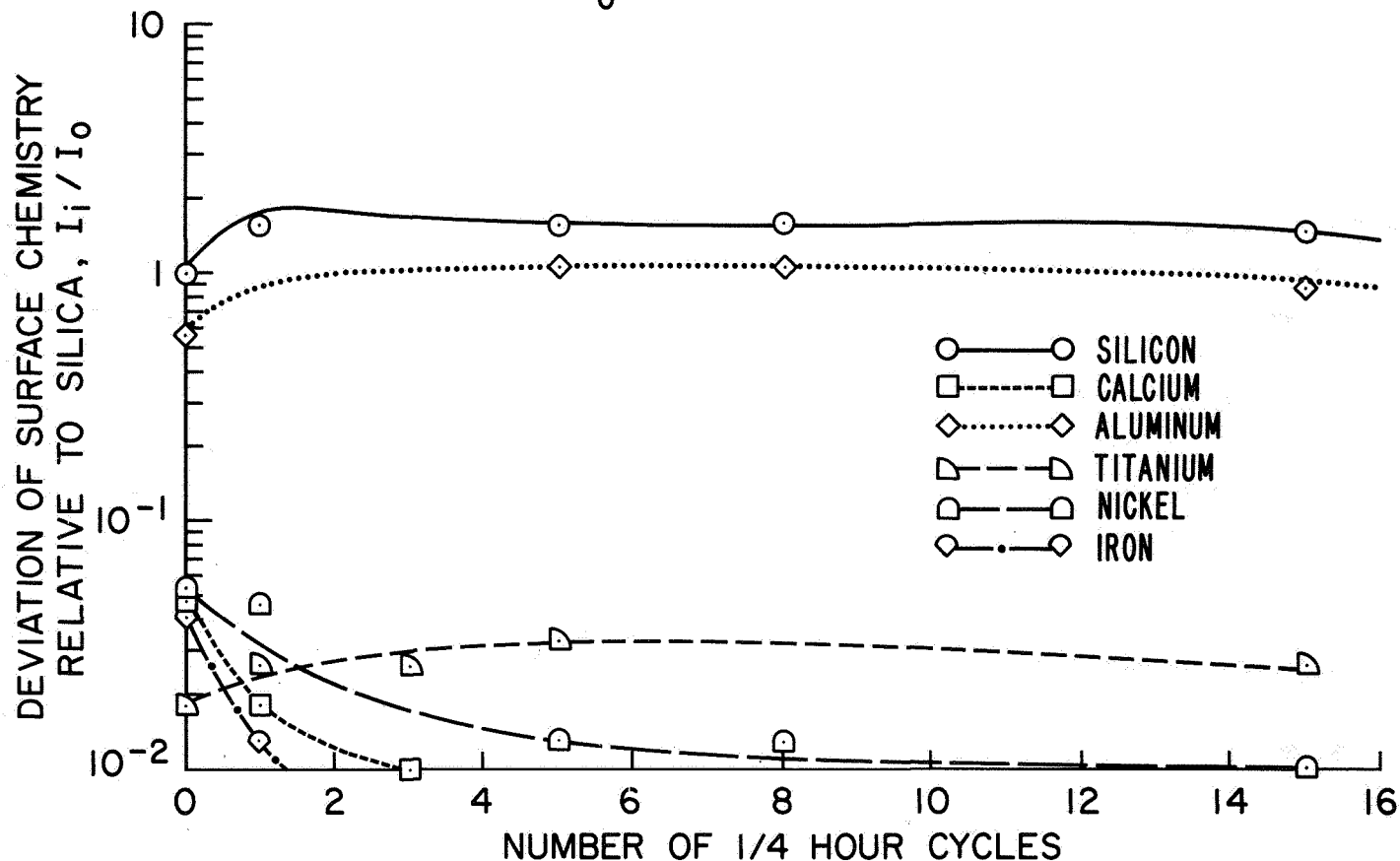


Figure 13

CHANGE IN SURFACE COATING CHEMISTRY AFTER RADIANT HEAT TESTING  
REI-MOD 1A

(Figure 14)

This figure illustrates the changes in the surface chemistry that occur in the REI-MOD 1A coating as a function of radiantly heated cyclic tests at 1480°K. These tests were conducted at a pressure of 810 N/m<sup>2</sup> (0.008 atm), which was equivalent to the stagnation pressure in the convectively heated cyclic tests. The surface temperature achieved was about the same as that obtained at the 340 kw/m<sup>2</sup> heating rate during convective heating. The results indicate significant differences in surface chemistry behavior between the radiant heating tests and the convective heating tests illustrated in figure 12. Specifically, the relative concentration of nickel increases during radiantly heated cyclic tests while it decreases during convectively heated cyclic testing. This difference again indicates an interaction is occurring between the boundary layer present during convective heating and the REI-MOD 1A coating that does not occur in radiant heating. The increase in relative concentrations of nickel, aluminum, and silicon is again probably due to the loss of lithium from the coating, which is not detectable with this analytical technique. The concentrations of other minor constituents present in the coating that decrease during convective heating remain constant during the radiant heating tests.

# CHANGE IN SURFACE COATING CHEMISTRY AFTER RADIANT HEAT TESTING

REI - MOD 1A

$T_w \approx 1480^\circ \text{ K}$        $P_s = 810 \text{ N/m}^2$

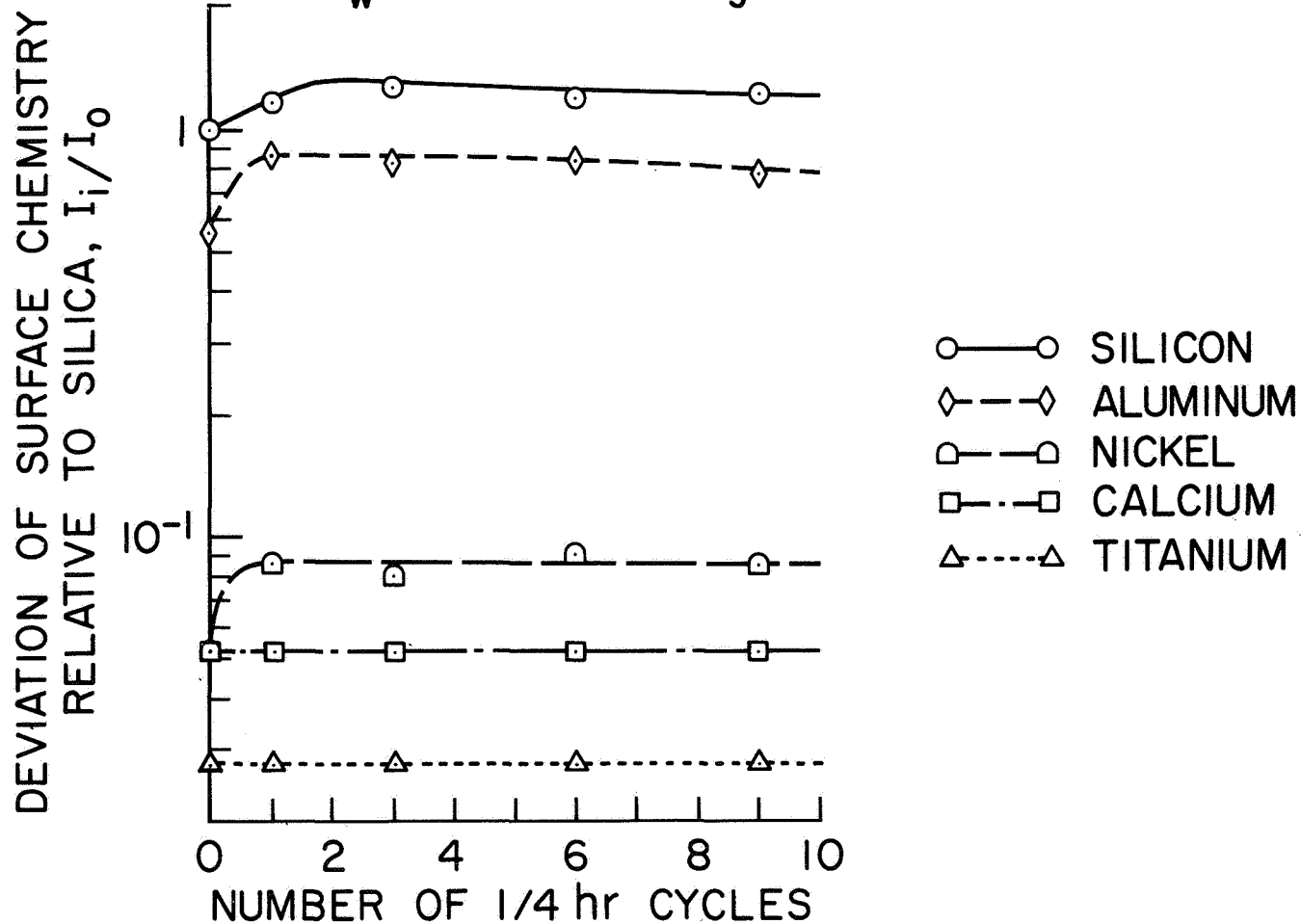


Figure 14

## CHANGE IN SURFACE COATING CHEMISTRY AFTER ARC PLASMA TESTING

LI-1542

(Figure 15)

This figure illustrates the change in surface coating chemistry of the LI-1542 coating that occurs as a function of convectively heated cyclic testing, at the  $340 \text{ kw/m}^2$  heating rate. The results indicate little change in chemical composition of the LI-1542 coating after one cyclic test. This result is partly due to the fact that this coating contains no elements other than silicon, carbon, oxygen, and boron in large enough concentrations to be significant, and, therefore, detectable. The increase in concentration observed after one cycle is probably the result of two factors. The first one is the change in the surface morphology (densification) of the coating itself, which occurred within one cycle. The second one is the loss of some of the minor constituents of the untested coating, primarily boron, which is undetectable with this particular analytical technique. A similar surface chemistry response was observed at the  $450 \text{ kw/m}^2$  heating rate.

# CHANGE IN SURFACE COATING CHEMISTRY AFTER ARC PLASMA TESTING

LI-1542

$$\dot{q} = 340 \text{ kW/m}^2$$

$$H_{e0} = 10.7 \text{ MJ/kg}$$

$$P_s = 810 \text{ N/m}^2$$

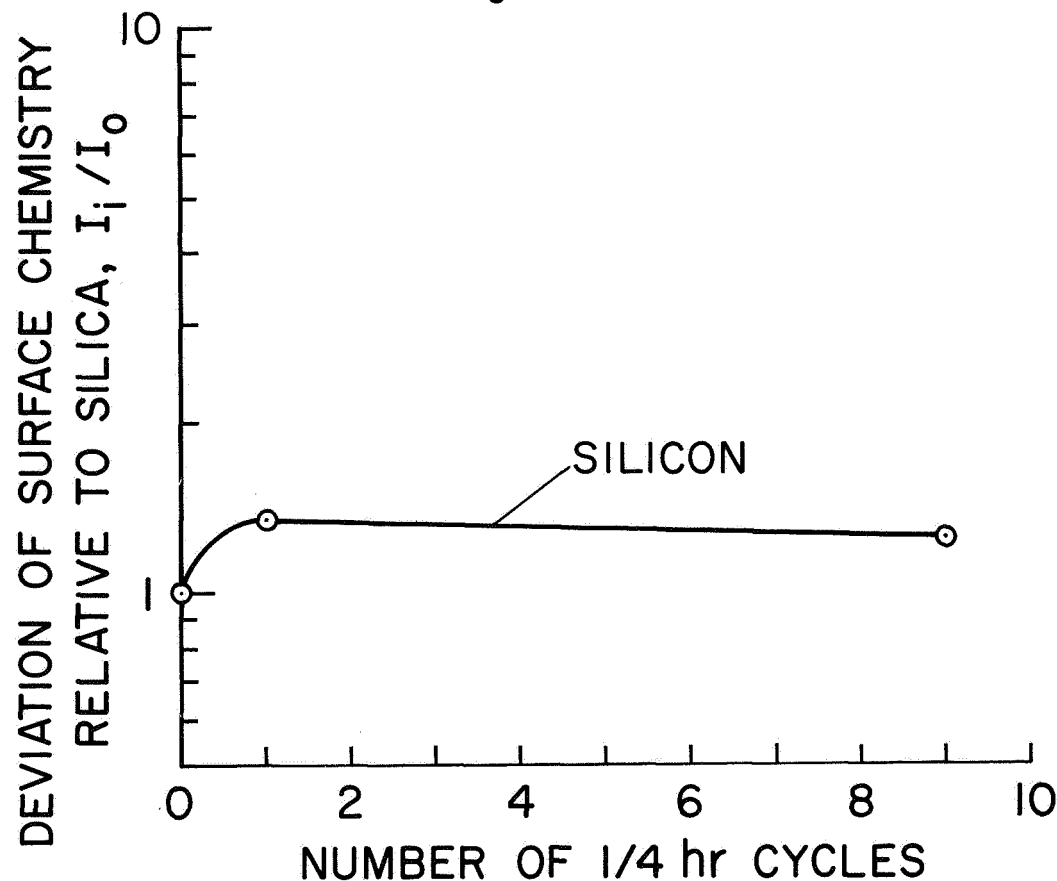


Figure 15

X-RAY FLUORESCENCE CHEMICAL ANALYSIS OF HCF-MOD III COATING  
CROSS SECTION - PRETEST

(Figure 16)

This figure illustrates a chemical analysis of the HCF-MOD III coating in cross section before testing. It was obtained by the method described in figure 7. The analysis was taken through a strip 25 microns wide, which is illustrated by the white lines superimposed upon the scanning electron micrograph in the figure. These results are semiquantitative and uncorrected for absorption of X-rays, which will occur due to the elements present in the coating. The components of the individual layers of this coating are illustrated in this figure. The spatial response of the instrument is indicated by the shaded areas on the plots in the figure. The top layer is composed primarily of cobalt and iron with chromium and silicon also evident. Data for potassium, which is also present in the top layer, are not presented due to a sample preparation problem, which made the data unreliable. The intermediate layer is composed primarily of chromium and silicon. The bottom layer is primarily composed of aluminum and silicon.

# X-RAY FLUORESCENCE CHEMICAL ANALYSIS OF HCF-MOD III COATING CROSS SECTION - PRETEST

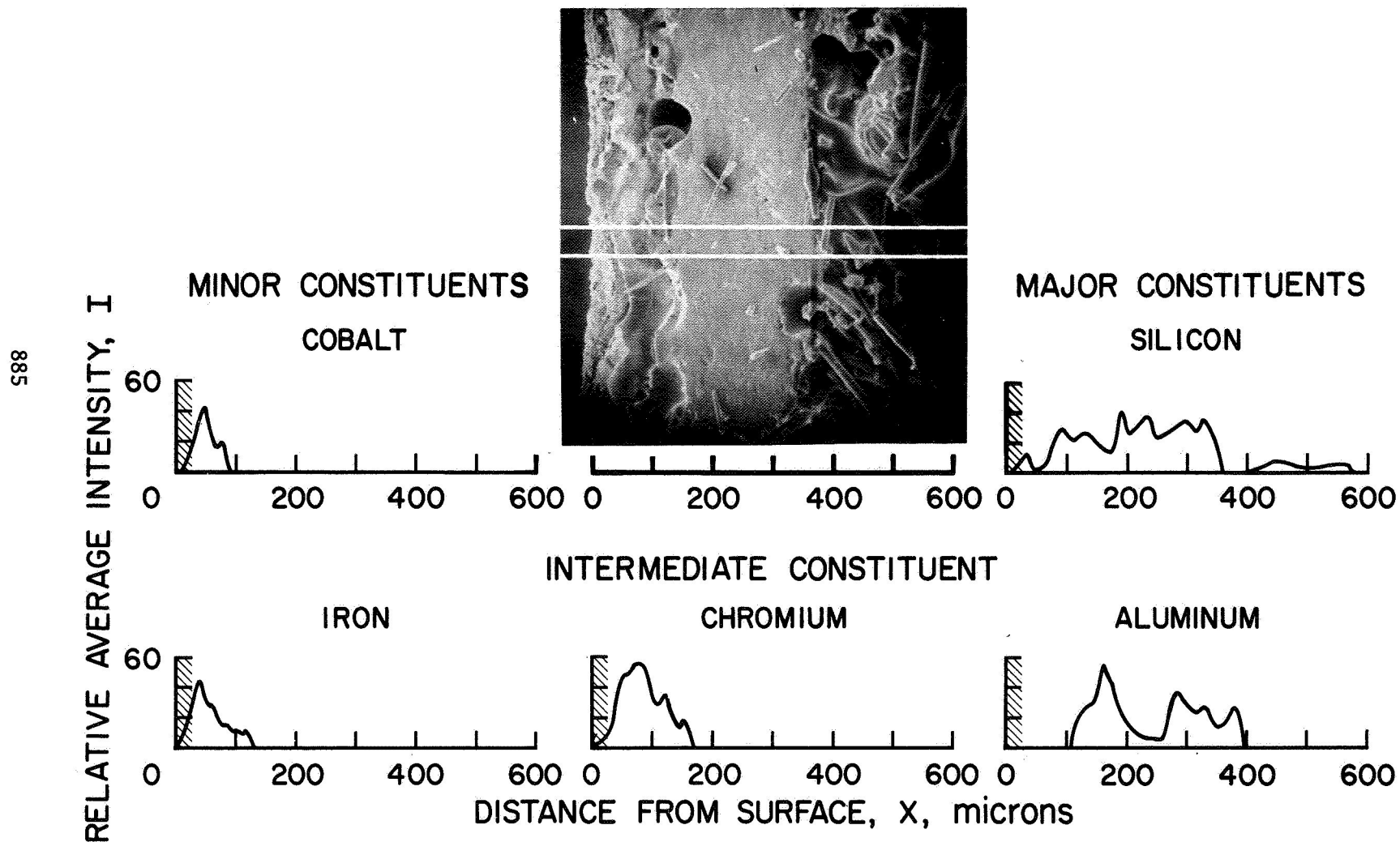


Figure 16

X-RAY FLUORESCENCE CHEMICAL ANALYSIS OF HCF-MOD III COATING  
EXPOSED TO ARC PLASMA ENVIRONMENT AFTER 8 CYCLES

(Figure 17)

The analysis of the HCF-MOD III coating in cross section after eight cycles at the 340 kw/m<sup>2</sup> heating rate is illustrated in this figure. When this coating is compared to the pretest coating, figure 16, several changes are noted. The loss of cobalt and iron from the top layer coincident with the loss of the top coating is the most significant result. The appearance of chromium and aluminum closer to the surface is also indicative of the surface recession of the coating.



# X-RAY FLUORESCENCE CHEMICAL ANALYSIS OF HCF-MOD III COATING EXPOSED TO ARC PLASMA ENVIRONMENT AFTER 8 CYCLES

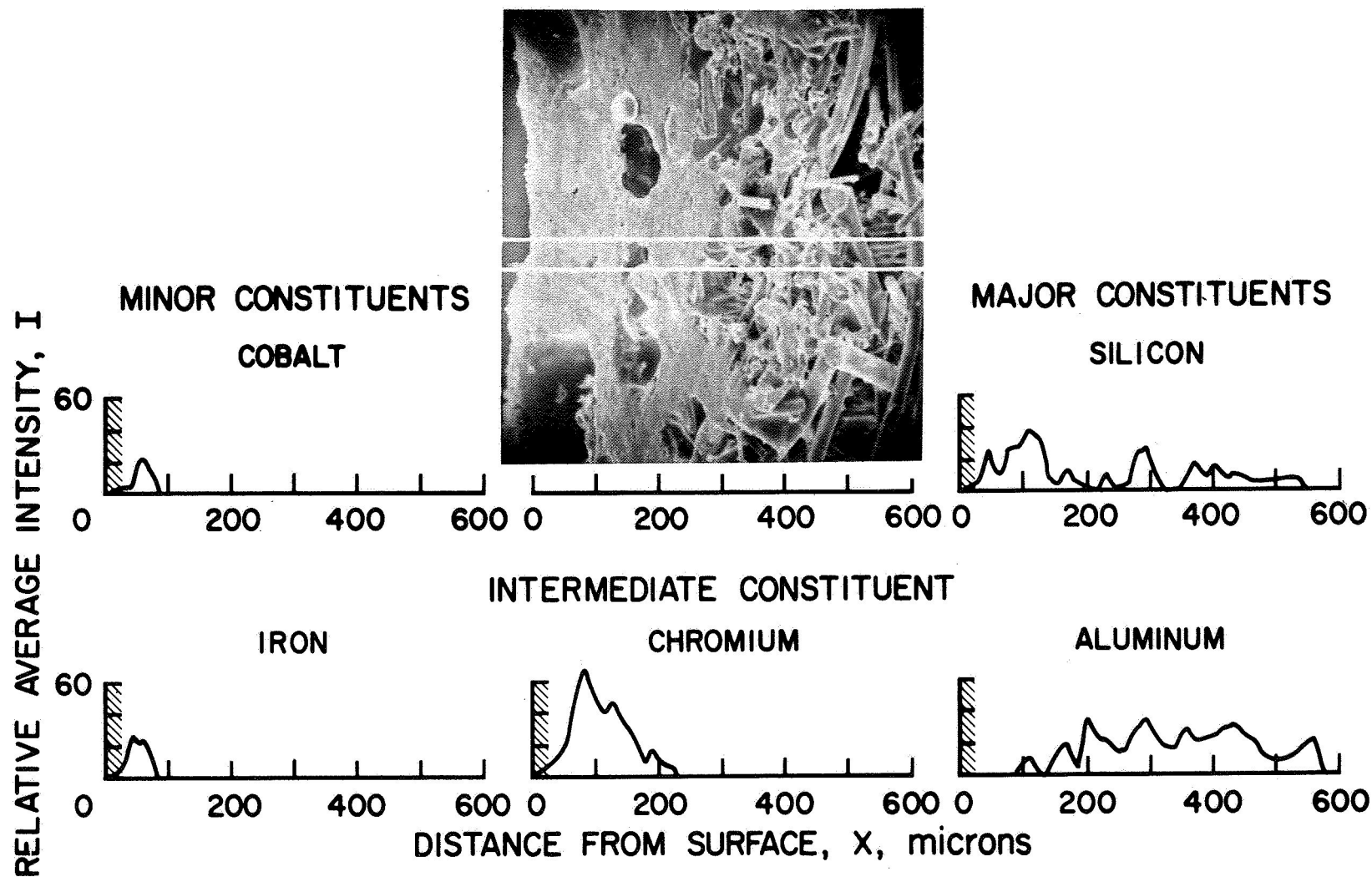


Figure 17

X-RAY FLUORESCENCE ANALYSIS OF CROSS SECTION OF REI-MOD 1A COATING  
PRETEST

(Figure 18)

This figure illustrates the analysis of the REI-MOD 1A coating in cross section before testing. Although the results of this analysis indicate that the elements in the coating (nickel, titanium, aluminum, and silicon) are, in general, uniformly distributed, some areas of non-uniformity exist. Analysis for lithium, one of the major constituents of the coating, was not obtainable using this technique.

X-RAY FLUORESCENCE ANALYSIS OF CROSS SECTION OF  
REI-MOD 1A COATING  
PRETEST

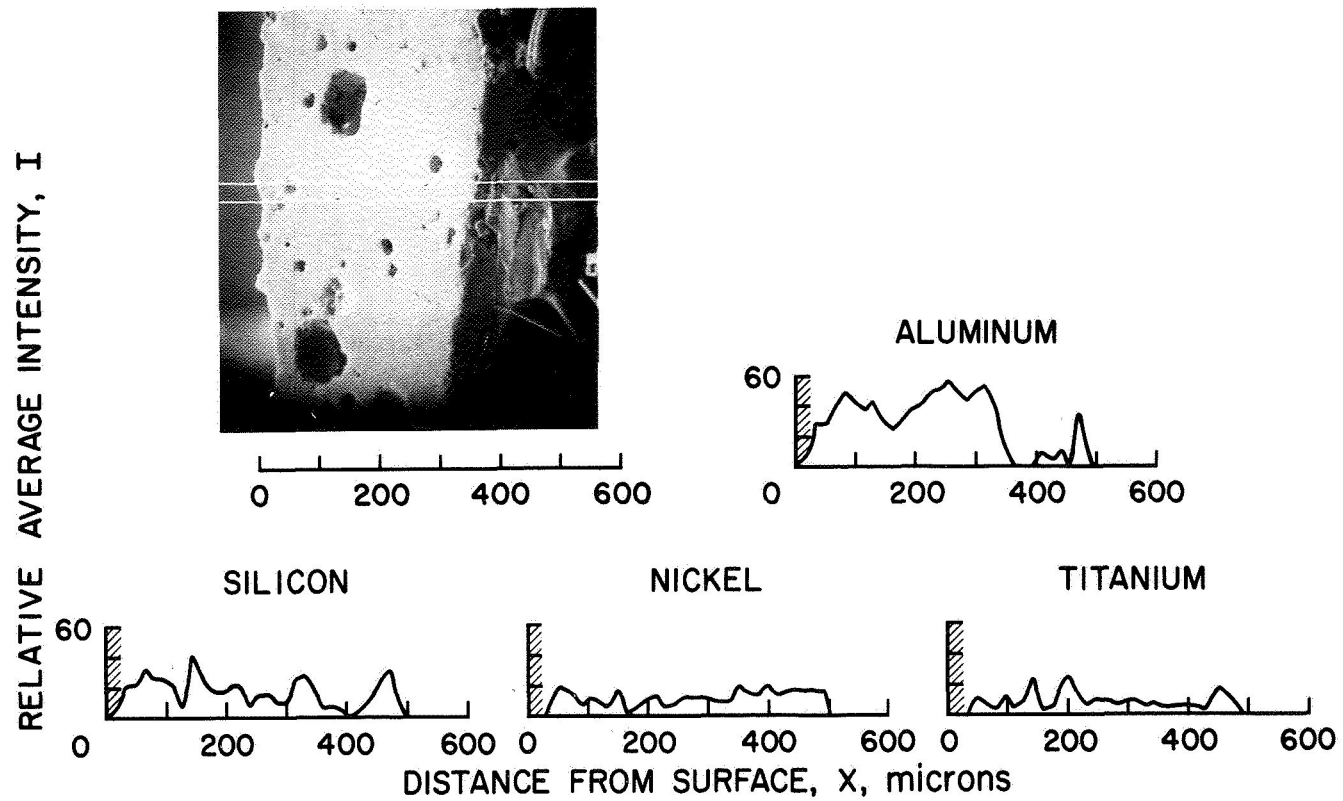


Figure 18

X-RAY FLUORESCENCE ANALYSIS OF CROSS SECTION OF REI-MOD 1A COATING  
AFTER 8 CYCLES

(Figure 19)

An analysis of the REI-MOD 1A coating in cross section after eight cycles at the 340 kw/m<sup>2</sup> heating rate is illustrated in this figure. Little change in the location of components within the initially uniformly distributed coating is noted although it does appear that titanium is beginning to diffuse toward the surface. The difference between the top layer of the coating and the coating, in general, is still visible in the scanning electron microscope although no chemical difference can be found between the two layers utilizing this type of analytical technique. The change in appearance may be partly attributable to the loss of lithium from the coating, which cannot be detected with this technique, and to an increased foaming of the glass surface.

# X-RAY FLUORESCENCE ANALYSIS OF CROSS SECTION OF REI-MOD 1A COATING AFTER 8 CYCLES

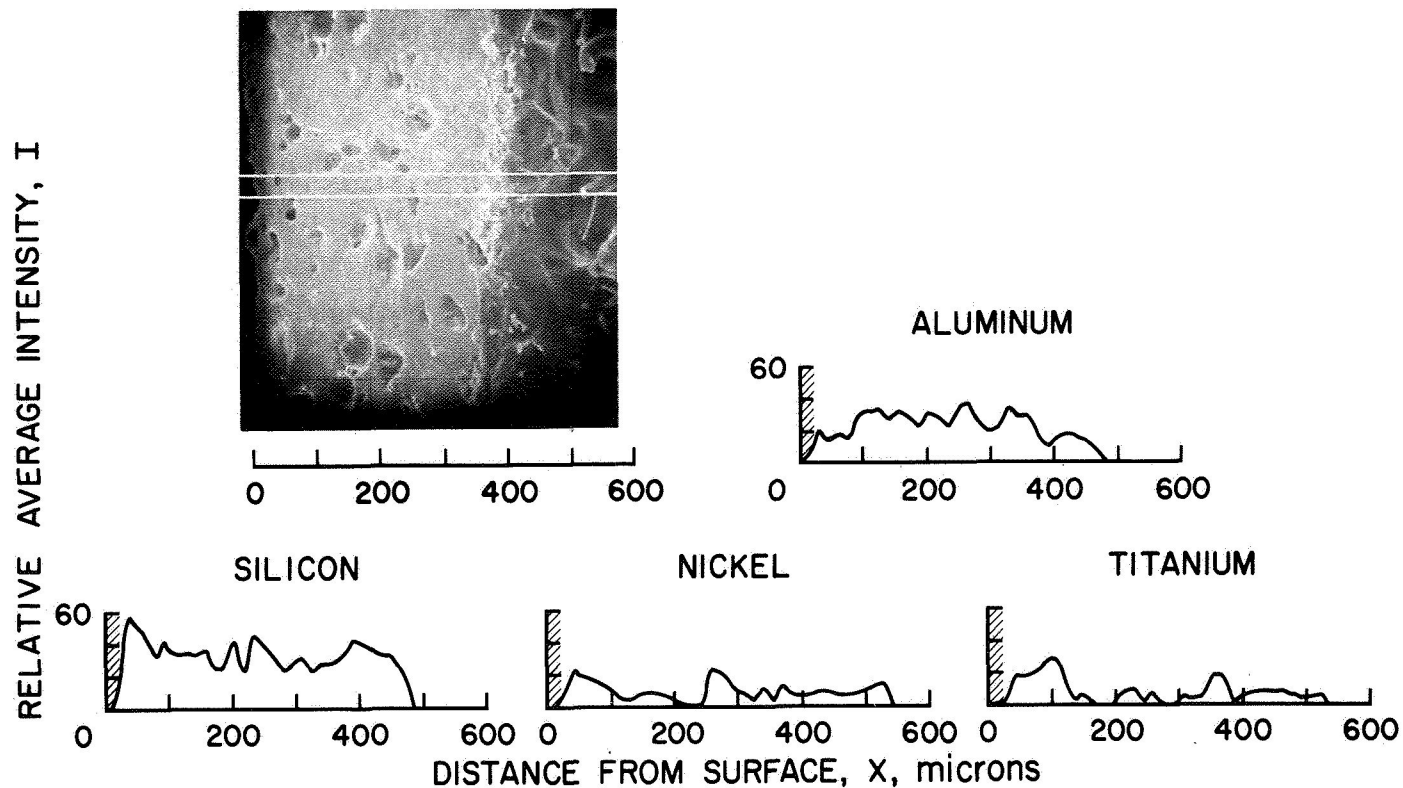


Figure 19

## CONCLUSIONS

(Figure 20)

The response of RSI coatings to a convective heating environment has been described in terms of the morphological and surface chemistry changes that occur after cyclic testing. The loss of high vapor pressure molecular species to the convectively heated environment has been described for the HCF-MOD III and REI-MOD 1A coatings. The LI-1542 coating is also probably losing volatile species which are not detectable with the analytical techniques utilized but only to a limited extent. Each coating's reaction to the convectively heated environment was unique with the HCF-MOD III exhibiting the most significant response while the LI-1542 coating exhibited the least. The most significant result is that the response of RSI coatings to a radiant heating environment which is normally used to simulate the thermal history of space shuttle's reentry is chemically different from the coating's response to a convectively heated environment. This conclusion indicates, in particular, that the effect of convective heating on coatings must be evaluated in an arc plasma environment, rather than in a radiant heating environment.

## CONCLUSIONS

- THE LOSS OF HIGH VAPOR PRESSURE MOLECULAR SPECIES TO THE CONVECTIVELY HEATED ENVIRONMENT IS OBSERVED IN HCF-MOD III COATING AND RESULTS IN A MEASURABLE AMOUNT OF SURFACE RECESSION.
- THE LOSS OF HIGH VAPOR PRESSURE MOLECULAR SPECIES TO THE CONVECTIVELY HEATED ENVIRONMENT IS OBSERVED ON THE REI-MOD IA SURFACE BUT NO MEASUREABLE SURFACE RECESSION IS OBSERVED.
- THE HCF-MOD III COATING EXHIBITS THE MOST SIGNIFICANT CHEMICAL AND MORPHOLOGICAL CHANGES WHEN EXPOSED TO A CONVECTIVELY HEATED ENVIRONMENT.
- THE REI-MOD IA APPEARS TO FOAM IN RESPONSE TO THE CONVECTIVELY HEATED ENVIRONMENT.
- THE LI-1542 COATING EXHIBITS THE LEAST CHEMICAL AND MORPHOLOGICAL CHANGES WHEN EXPOSED TO A CONVECTIVELY HEATED ENVIRONMENT
- RSI COATING RESPONSE TO RADIANT HEATING IS DIFFERENT THAN TO CONVECTIVE HEATING.

Figure 20

## REFERENCES

1. Tanzilli, R.A. (Ed.): Development of an External Ceramic Insulation for the Space Shuttle Orbiter. NASA-CR-112038, April 1972.
2. Buttram, R.D., Space Shuttle Thermal Protection System Development. Final Report, January 17, 1972, NAS9-12083.
3. Lehman, J.K., Rusert, E.L., Kummer, D.L. and Christensen, H.E.: Reusable Surface Insulation (RSI) Thermal Protection Development for Shuttle. Final Report, March 21, 1972, NAS9-12082.